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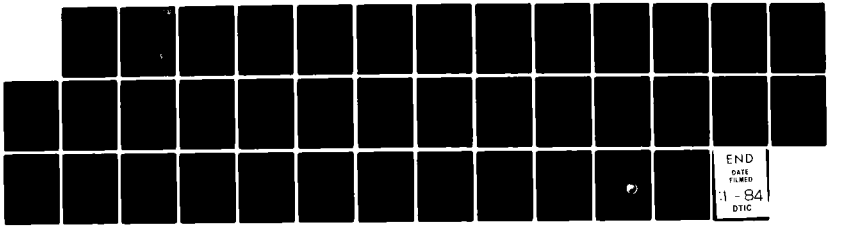

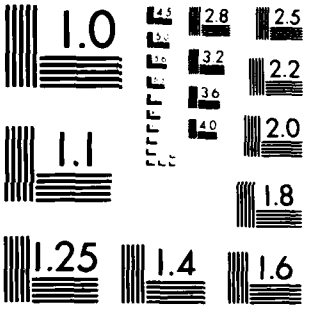

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GEO-CENTERS, INC.

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GC-TR-82-291

# INTRINSIC AND EXTRINSIC PROPERTIES OF FIBER OPTIC SENSOR MATERIALS

Prepared for:

U.S. NAVAL RESEARCH LABORATORY
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Contract Number N00014-82-C-2326



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September 1983

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# INTRINSIC AND EXTRINSIC PROPERTIES OF FIBER OPTIC SENSOR MATERIALS

## I. INTRODUCTION

In recent years, considerable interest has been focused on the development of a second generation of fiber optic materials. This interest has been sparked by the prediction that heavy metal halide glasses possess intrinsic transparencies several orders of magnitude greater than oxide glasses and will offer the promise of greatly increased repeater spacing for optical communication systems. Of a number of candidate halide glasses having high intrinsic optical transparency, the $ZrF_4$-$BaF_2$-$LaF_3$-$AlF_3$ glass system, modified with LiF for increased stability and with $PbF_2$ for refractive index control, has demonstrated the predicted $\lambda^{-4}$ wavelength dependent scattering loss.[1] Bulk glasses of this composition have demonstrated extrapolated scattering losses of $2.7 \times 10^{-3}$ dB/km at 4 μm. This loss value is about a factor of 2 higher than the projected theoretical level.

The discovery of this composition was a necessary first step in the development of ultra-low loss fibers. The transition from a bulk glass having an ultra-low extrapolated scattering loss to an optical fiber having an actual absorption loss of comparable value is a difficult task, requiring the identification and elimination of sources of extrinsic absorption and scattering loss in the raw materials and glasses, and the development of processes suitable for transforming the bulk material to the fiber form without significantly increasing the inherent optical attenuation of the glass.

This report summarizes the progress made in this task and specifically focuses on three areas identified as essential to the development of ultra-low loss halide glass fibers.

1. Identification and elimination of extrinisic absorption and scattering losses.
2. High quality preform preparation.
3. Loss minimization during fiber drawing.

## II. RAW MATERIAL CHARACTERIZATION

The intrinsic absorption minimum for glasses of the $ZrF_4$ system occurs in the 3 to 4 μm region. This region of maximum transparency lies at the intersection of the wavelength dependent Rayleigh scattering loss curve and the multiphonon absorption edge. A number of chemical species are known to increase the absorption within this region of minimum loss. The first is comprised of the di-valent transition elements Cu, Fe, Ni, Co which have been shown to cause absorption losses as high as 130 dB/km in the 1 to 3 μm region when present in halide glasses at the 1 ppm level.[2] The second group, hydroxides and hydrates, show an intense absorption band centered at 2.9 μm. This absorption is attributable to the M-OH stretching mode and is characteristic of metal hydroxides as well as hydrates and surface absorbed water. A third group, oxides, do not absorb within this region but indirectly increase absorption by causing a shift in the multi-phonon edge to a shorter wavelength, thus forcing the minimum up the Rayleigh scattering loss curve. The first overtone for oxides in halide glasses was found at 7.4 μm for samples of the NRL composition spiked with

both $ZrO_2$ and $La_2O_3$.[3] Analytical methods have been developed to detect the presence of these sources of absorption loss in the raw materials and glasses and processes have been developed to minimize their concentrations.

Sources of Transition Element Impurities

A systematic quantitative and qualitative analytical study using a DC Plasma Spectrometer (Beckman Instruments, Inc.) has been conducted to identify the sources of transition element impurities in the bulk glasses prepared at NRL.[4] In-house prepared raw materials were analyzed for each transition element. In the lanthanum and zirconium fluoride, Fe was found at the 1 ppm level while the other elements were present at approximately .1 ppm each. All other matrix components had impurity concentrations at or near the analytical detection limit of 20 ppb. Since $ZrF_4$ is the major constituent at ~ 50 mole %, it is the major source of transition element impurities. A thorough analysis of each step in the preparation of this compound indicated that the source of the iron impurity was contaminated $ZrOC\ell_2$. Successive recrystallizations failed to decrease the Fe content of $ZrOC\ell_2$ after the first recrystallization.

The use of high purity (< 5 ppb Fe) concentrated $HC\ell$ did not significantly reduce the Fe concentration in re-precipitated $ZrOC\ell_2$, indicating that iron is probably preferentially absorbed onto or occluded into the precipitate. A new purification technique, selective for both Fe and Cu, was found to reduce these impurities to the 10-25 ppb level in

$ZrOC\ell_2$. This process offers an alternative and substantially improved method for the preparation of high purity $ZrOC\ell_2$. If the subsequent processing steps for the conversion of the oxychloride to the fluoride do not contaminate the material, absorption losses due to iron and copper impurities in the glass should drop to below the 1 dB/km level in the 2 to 3 μm wavelength region.

A number of commercial sources of $ZrF_4$ (CERAC, ALFA, BDH, RARE EARTH METALLIC) were also analyzed and total transition element levels ranged from 10 ppm to several thousand ppm. It is apparent that no commercial sources of higher purity than NRL prepared materials are yet available.

Hydroxide and Hydrate Contamination

The OH vibrational absorption band at 2.9 μm is the single most difficult obstacle to attaining ultra-low loss fibers from the halide glass system. Differential thermal analysis (DTA) of all NRL-prepared starting materials reveals that $ZrF_4$ and $BaF_2$ contain significant amounts of water bound chemically as the hydrate. Further study indicates that these compounds undergo an endothermic reaction as they are heated indicating either dehydration or irreversible chemical transformation. If the latter reaction occurs in the case of $ZrF_4$, it is likely that hydroxides, oxy-hydroxides, and oxyfluorides are formed. In addition to the presence of water in the raw materials, a second source of OH contamination has been identified as originating from exposure of the melted glass to water vapor. This can occur during melting or quenching.

This latter observation indicates that all glass processing must be performed in a relatively water-free atmosphere to eliminate OH contamination. Two processes have been developed to reduce OH contamination of the fluoride glass. The first involves the use of a reactive atmosphere designed to convert hydroxides to fluorides by the presence of free fluorine generated over the melted glass by the decomposition of either $CF_4$ or $SF_6$.[5] Using this method, reprocessed glasses having bulk OH absorption bands < 2000 dB/km have been prepared. A second process using an inert atmosphere of Argon containing less than 10 ppm of $H_2O$ has successfully reduced the OH band to < 1000 dB/km. With both processes, the ultimate OH level may be determined by the actual level of water contamination in the environment in which the glass is processed.

The OH absorption band intensities given for both processes are upper limits determined on bulk glasses. More precise values will be available when absorption spectra for fibers prepared from glasses processed using these OH reducing procedures become available.

Several other RAP systems utilizing $CC\ell_4$, $I_2$, HF, $Br_2$ as reactive gases were studied and were found to be less effective in reducing OH absorption than the $CF_4$ and $SF_6$ processes.[6]

## Oxide Impurities

The observed oxide induced multiphonon edge shift has been found to be dependent on the history of the glass sample.[3] Glasses prepared from raw materials processed with ammonium bifluoride, quenched, and then remelted, tend to show less intense oxide bands when spiked with 1 wt %

$ZrO_2$ or $La_2O_3$ than do glasses prepared without ammonium bifluoride. This observation indicates that HF is retained in the melt and successfully converts the added oxides to fluorides during the remelting process. It is also expected that oxides and hydroxides, generated from the decomposition of hydrates in the raw materials will also be converted to fluorides by the RAP process described above, thus reducing the attenuation increase due to multiphonon edge shift.

Sources of Extrinsic Scattering Losses

A major factor preventing the attainment of the theoretical predicted minimum loss is the presence of extrinsic scattering due to the formation of crystallites in bulk glasses and preforms prepared by casting techniques. An intensive study has been conducted to characterize a number of these crystallites so that processing and minor compositional changes can be made in order to avoid devitrification.[7]

Optical microscopy with transmitted polarized light was found to be the most useful technique for rapid characterization of the degree of crystallization and identification of the crystal habit. Micro x-ray diffraction analysis coupled with x-ray fluorescent analysis has successfully been used to identify a commonly found cubic crystal as $AlF_3$ while two other different crystal morphologies have been identified as $LaF_3$. These observations indicate that a minor reduction in the $AlF_3$ and $LaF_3$ content of the glasses may be needed in order to prevent devitrification.

Two additional sources of extrinsic scattering have been identified. Melts exposed to water vapor during quenching tend to yield glasses having a lower glass stability. Oxides added to stable glass melts

likewise cause devitrification at concentrations as low as .2 wt %. The additional scattering from both sources may originate from oxyfluoride formation. The processes for the reduction in scattering arising from these sources have been discussed in detail in previous sections.

## III. PREFORM PREPARATION METHODS

Achieving successful waveguide structure is dependent on the development of compatible core and clad glasses as well as configuring these glasses as a cylindrical preform with a high degree of concentricity. The configuration process can be accomplished in a variety of ways. However, the most satisfactory method reported to date is a rotational casting technique developed at NRL in 1982.[8] This process represents a substantial advance in the state-of-the-art of preform fabrication for fluoride glasses.

In this innovative process, a molten cladding glass is poured into a heated metal mold which is spun horizontally and gradually cooled until a fluoride glass tube is formed. Tubes prepared in this manner are found to be extremely uniform over the entire length of the sample. Core glass can then either be poured into the hollow tube or drawn into it under a vacuum. The result is an extremely high quality preform. The mechanical apparatus used for mold rotation is a modified lathe capable of generating 5000 rpm within a few seconds and which can fit into the controlled atmosphere glove box, thus allowing preform fabrication in an inert, water-free atmosphere.

Additionally, a vapor phase approach, termed reactive vapor transport process (RVT), has been investigated for preform preparation.[9]

Refractive index profiles obtained from preforms prepared via this novel technique indicates that both multimode graded-index and monomode fluoride fiber waveguides can be readily prepared.

## IV. MINIMIZATION OF INDUCED DRAWING LOSS

Total optical loss of drawn fibers is the sum of intrinsic scattering loss, drawing-induced losses, and extrinsic absorption and scattering losses associated with material impurity levels, glass processing, core-clad interface imperfections, etc. The minimizati of drawing-induced losses requires that parameters such as preform fee rate, fiber take-up rate, drawing temperature control, and hot-zon length be optimized. To evaluate drawing loss, a number of preform ere prepared by polishing rods cut from non-cast glasses, rods cast in a gold coated mold and glass cladded preforms prepared by the rotational casting process. Preliminary draws indicated that samples not cladded with teflon FEP tended to crystallize at the rod neck-down and yielded exceptionally (> 10000 dB/km) lossy fibers. The cause for this crystallization is thought to be due to either water vapor induced nucleation or nucleation initiated by the mechanical stresses of glass expansion and contraction as the glass passes thru the hot-zone region. In addition, a hot-zone greater than 5 to 7 mm in length generally caused high induced scattering. A furnace redesign allowing for atmosphere controlled RF heating at the neck-down is being implemented.[10]

Using a reduced hot zone length (5 to 7 mm) with an optimum drawing temperature of 303°C at a drawing speed of 5 m/min, fibers of 315 μm overall diameter were obtained from an FEP cladded highly polished

fluoride glass rod of 13 mm diameter. Scattering loss measurements for these fibers verified Rayleigh behavior. The extrapolated Rayleigh scattering loss was determined to be .012 dB/km at 4 μm. A wavelength independent scattering off-set of 5.08 dB/km, due mainly to core-clad interface defects and due partly to higher-order cladding and leaky modes, was characteristic of the fibers drawn from that particular preform.[11]

Loss measurements of fibers drawn from similarly prepared rods showed bulk scattering losses only several times higher than the Rayleigh scattering loss of the bulk rod. These results indicate that even with a rather long hot zone and an uncontrolled atmosphere at the neck-down, drawing induced scattering is exceptionally low. Further reductions in induced scattering can be expected with use of the RF drawing furnace.

## V. CONCLUSIONS

The major sources of extrinsic absorption and scattering losses in fluorozirconate glasses and fibers have been identified. The origin of transition element impurities has been determined and a new separation process for their removal has been developed. A new reactive atmosphere process for reducing anion impurities is currently in use. Hydroxide contamination from atmospheric water has been recognized and glass processing and rod casting is being conducted in a specially designed atmosphere controlled glovebox. A recent modification will allow for the rotational casting of preforms within the glove box. Two processes suitable for preparing multimode preforms have been developed. Their

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applicability for single mode preform essential for long length repeaterless data transmission, appears promising. The extent of drawing induced scattering loss has been determined and its reduction can be expected with the use of atmosphere controlled RF furnace.

Continued reduction in total extrinsic loss can be expected as these techniques and processes are totally integrated into the low loss fiber program.

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## APPENDIX

Reprints of published articles generated by this research project follow.

# PREPARATION OF HEAVY METAL FLUORIDE GLASS OPTICAL FIBERS
## (A New Approach)

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A vapor phase approach, termed reactive vapor transport process (RVT), was investigated for the fabrication of fluoride glass optical fibers. The refractive index profiles, obtained from preforms prepared via the novel technique, indicate that both multimode graded-index and monomode fluoride glass fiber waveguides can be readily prepared.

The only method for making fluoride glass fibers known to date is to cast the fluoride glass melts.[1-3] The casting process appears to be limited to step-index fibers. In addition, careful examination of our cast preforms of substantial lengths (> 6 in) generally revealed density variations in the core and microcrystallites at the core-clad interface. These scattering defects have resulted in wavelength-independent fiber losses ranging from 5 dB/km[4] to several hundred dB/km. To avoid casting the melts, a reactive vapor or mixture of vapors originated from low vapor pressure metal halides or from halogenated gases, were carried inside a fluoride glass tube. With proper control of processing parameters such as temperature, time, and reactive vapor concentration, substantial amounts of chlorine, bromine, or iodine ions were exchanged and incorporated into the fluoride glass structure, thus raising the refractive index and forming a core region. A cross-section of a fluoride glass tube preform is shown in Fig. 1.

The difference in refractive indices $\Delta n = [n_f - n(b)]$ is plotted against b in Fig. 2, where $n_f$ represents the measured index at the inner wall of the tube and b is the overall tube wall thickness. The parabolic index profile suggests a diffusion controlled process. The index difference of Fig. 2

corresponds to a N.A. of only 0.045. However, in separate RVT experiments, it was demonstrated that N.A. > 0.1 and c (core wall thickness of Fig. 1) > 3 cm can be achieved. Optical characteriation of the core glass revealed a slight shift of the IR edge toward longer wavelengths, an appearance of two IR reflectivity bands at around 549 $cm^{-1}$ and 478 $cm^{-1}$, and a substantial decrease in the OH absorption band with respect to the cladding glass. All of these are attributed to the presence of Cl, Br, or I in the core glass structure. There was no microcrystals present at the core-clad interface.

In summary, a new fluoride glass fiber manufacturing process using reactive vapors was developed to suppress the extrinsic scattering loss generally observed in our substantially long cast preforms. In addition, the new approach allows (1) the modeling of the refractive index profile by varying the processing conditions, (2) the preparation of fluoride glass preforms having a very small core, (3) the prevention of OH contamination since reactive vapors are used, and (4) the prevention of contamination from dirt particles since it is an inside process.

Acknowledgments

The authors are grateful to Dr. P. Klein and Mr. C. Fisher for helpful comments and discussions and to Dr. G. Lu and Dr. K. Levin for the refractive index measurements.

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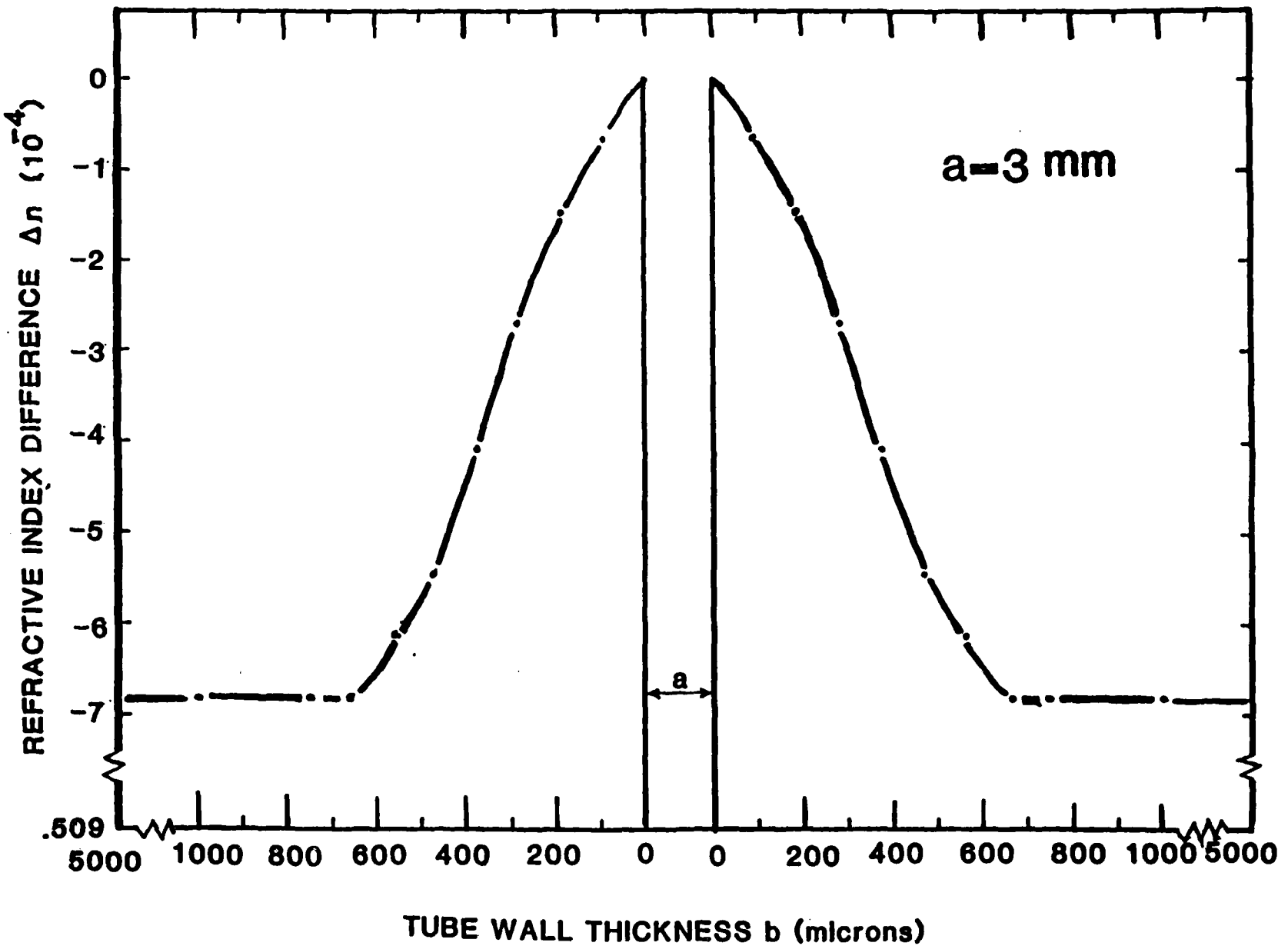
Figure Captions

Figure 1 Cross-section of a fluoride glass tube preform.

Figure 2 Index profile of a fluoride glass tube preform

[$\Delta n = n_i - n(b)$, where $n_i = n(0\ \mu m) = 1.5090$]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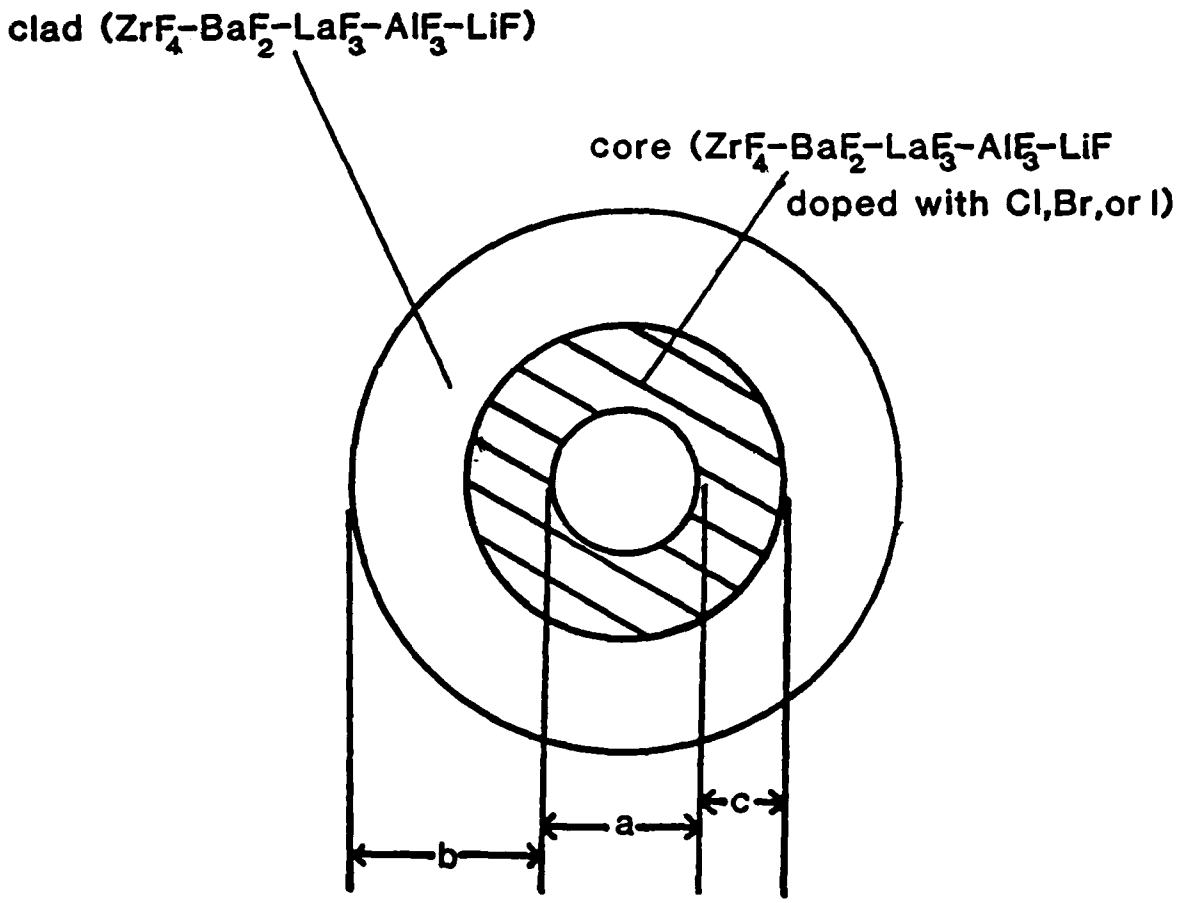
REFRACTIVE INDEX DIFFERENCE Δn (10⁻⁴)
0
-1
-2
-3
-4
-5
-6
-7
.509
a
5000 1000 800 600 400 200 0 0 200 400 600 800 1000 5000
TUBE WALL THICKNESS b (microns)


clad ($ZrF_4$-$BaF_2$-$LaF_3$-$AlF_3$-LiF)
core ($ZrF_4$-$BaF_2$-$LaF_3$-$AlF_3$-LiF
doped with Cl,Br,or I)
a
b
c

# TRACE IMPURITY ANALYSIS OF FLUORIDE GLASSES AND MATERIALS

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A number of selected instrumental techniques applicable for the qualitative and quantitative analysis of transition and rare earth element impurities at the ppb to ppm concentration levels in raw materials and final glasses is discussed. Chemical problems associated with reagent impurities, material solution, matrix-impurity separation and impurity reconcentration are outlined. Preliminary results for analysis by D.C. plasma spectro-photometry of selected transition and rare earth elements in glasses, in raw materials from various commercial sources, and in laboratory prepared materials purified by sublimation and solution recrystallization are presented.

Transition metal impurities at the 1 ppm level in fluoride glasses have been shown to cause extrinsic absorption losses as high as 130 dB/km in the 1 to 3 u region.[1] The presence of impurities at this concentration level in fibers is evident in the loss spectra of a recently reported fiber drawn at NRL which had an absorption loss in the same wavelength region of from 50 to 100 dB/km.[2] Future progress in reducing the total attenuation loss of fluoride glass fibers is very likely to be dependent upon the elimination of the sources of these impurities. The task of identification, quantification and elimination requires the judicious choice of a suitable analytical instrument and the development of analytical techniques capable of providing data routinely at the sub-ppm level. Of the various instruments available, DC plasma spectrometry offers a number of advantages over other methods such as ICP, atomic absorption, mass spectra and uv-visible spectrometers. Employing this analytical method, we have evaluated the purity of a number of commercial

sources of fluoride glass reagents and several in-house purified materials.

Commercial sources of $ZrF_4$, a major component of the NRL glass composition, ranged in impurity levels from several thousand ppm to 10 ppm. Iron was generally found at an order of magnitude greater than the concentration of Cu, Co or Ni. No commercial source having 1 ppm or less of iron was found for this material. Lanthanum oxide from two sources had iron concentrations at the 1 ppm level. Barium carbonate, lithium carbonate and aluminum oxide -- reagents from which fluorides can be readily prepared -- showed impurity levels at less than a few hundred ppm.

These data indicate that the major source of transition element impurities in fluoride glasses of the NRL composition prepared from commercially available reagents originate with the $ZrF_4$ component. Purification by multiple sublimations of this reagent can reduce the Fe impurity content to the 5-10 ppm level.

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# FLUORIDE GLASS FIBERS WITH ULTRA-LOW INTRINSIC LOSSES

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## Abstract

Recent advances in ultra-low attenuation waveguides are reported including development of stable fluoride glasses, efficient removal of OH ions, fabrication of large, uniform preforms and kilometer length fibers, and reduction of light scattering to near intrinsic levels.

# FLUORIDE GLASS FIBERS WITH ULTRA-LOW INTRINSIC LOSSES

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Recent advances in the area of non-silica based IR fiber waveguides have led toward the emergence of multi-component $ZrF_4$ based glass fibers as leading candidates for ultra-low loss fiber applications.[1,2] This paper will summarize the very significant technical progress we have made recently towards achieving the projected ultimate minimum loss of $10^{-3}$ dB/km in fluoride glass fibers. This includes the selection of stable, compatible, core-cladding fluoride glass compositions, the implementation of a rotational casting technique for uniform preform preparation, the substantial reduction of scattering losses to intrinsic Rayleigh scattering in bulk glass rods as well as in fibers, and the elimination of OH absorption by the melting of glasses in reactive atmospheres.

Fluoride glass compositions investigated were fundamentally three-component $ZrF_4$-$BaF_2$-$LaF_3$ systems but doped with LiF and/or $PbF_2$ to improve glass stability and viscosity-temperature characteristics which are essential for fiber drawing. The addition of LiF and $PbF_2$ largely increases the working range by > 13°C and decreases the activation energy for viscous flow to as low as 88 kcal/mole. The selected core-clad compositions also provide compatible expansion coefficients for preform fabrication and a high fiber numerical aperture of 0.2.

The rotational casting approach allows the preparation of a long-length concentric fluoride-glass cladding tube with precise control of the inner diameter. Fluoride glass preforms having controlled core/clad ratios can be obtained by casting the core melt into the tube, or alternatively, a rod and tube process can be applied.[3]

Direct measurements of light scattering losses in $ZrF_4$ based glasses as well as in fibers have verified that light scattering in highly stable fluoride glasses and fibers obeys the explicit $\lambda^{-4}$ Rayleigh behavior. The data project to an ultra-low minimum of 0.0027 dB/km and 0.01 dB/km, at 4 μm, for a 51.53 $ZrF_4$ - 20.47 $BaF_2$ - 5.27 $LaF_3$ - 3.24 $AlF_3$ - 19.49 LiF bulk glass and a 51 $ZrF_4$ - 16 $BaF_2$ - 5 $LaF_3$ - 3 $AlF_3$ - 20 LiF - 5 $PbF_2$ teflon-cladded fiber, respectively -- see Figures 1 and 2.

Substantial progress was also obtained in the reduction of OH absorption in fluoride bulk glasses and fibers. Using an $SF_6$ reactive atmosphere during melting, bulk OH content has been reduced to an estimated attenuation level of less than several hundred dB/km at 2.9 μm,[4] the peak of the OH fundamental absorption.

In summary, this paper reports for the first time the reduction of scattering losses to virtually intrinsic levels in zirconium fluoride-based glasses. In addition, OH levels have been dramatically lowered by reactive melting in $SF_6$ atmospheres. The combination of highly stable glass compositions, purification, and recently developed rotational preform casting techniques have permitted the fabrication of low loss fluoride glass fibers in lengths approaching 1 km.

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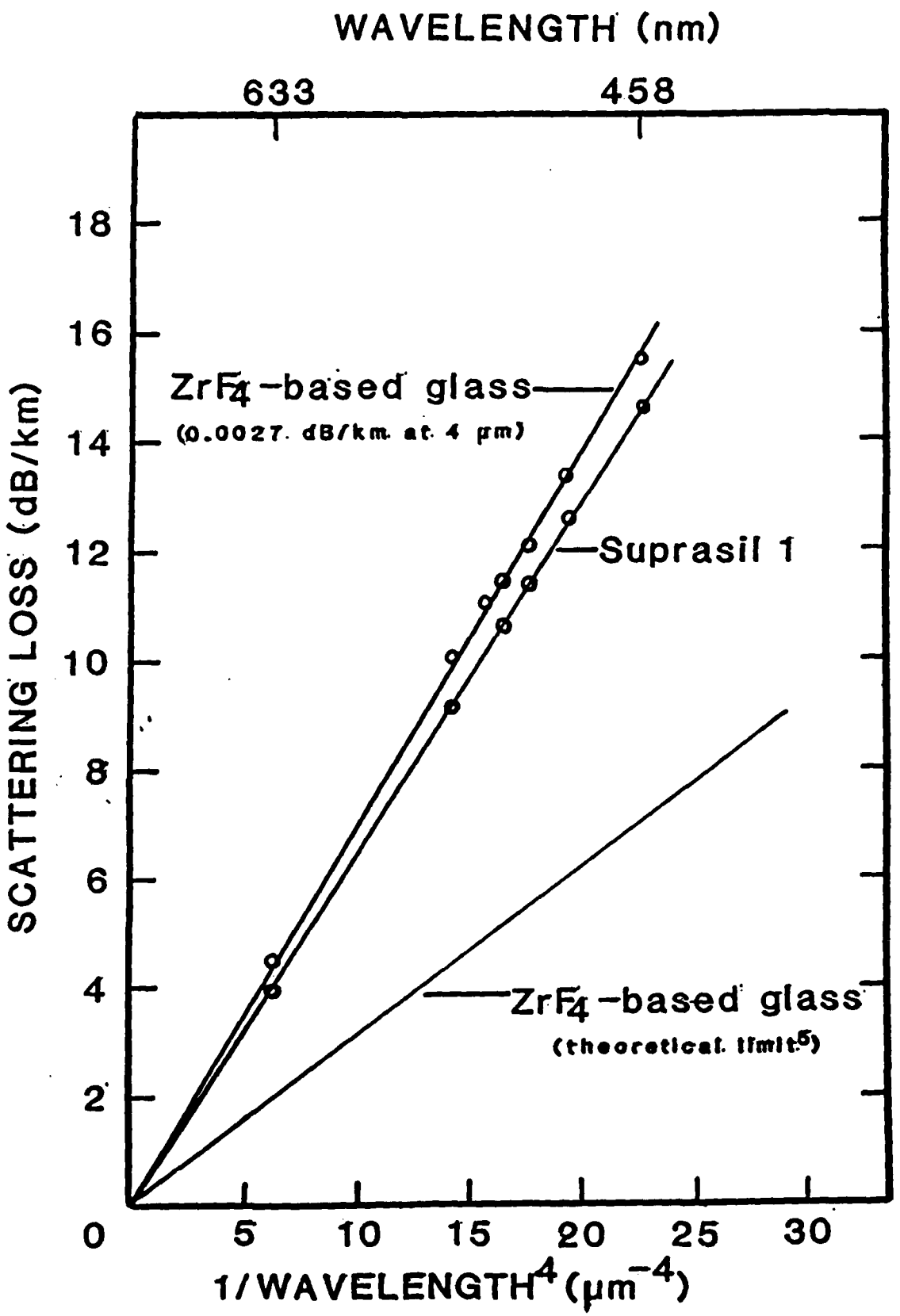
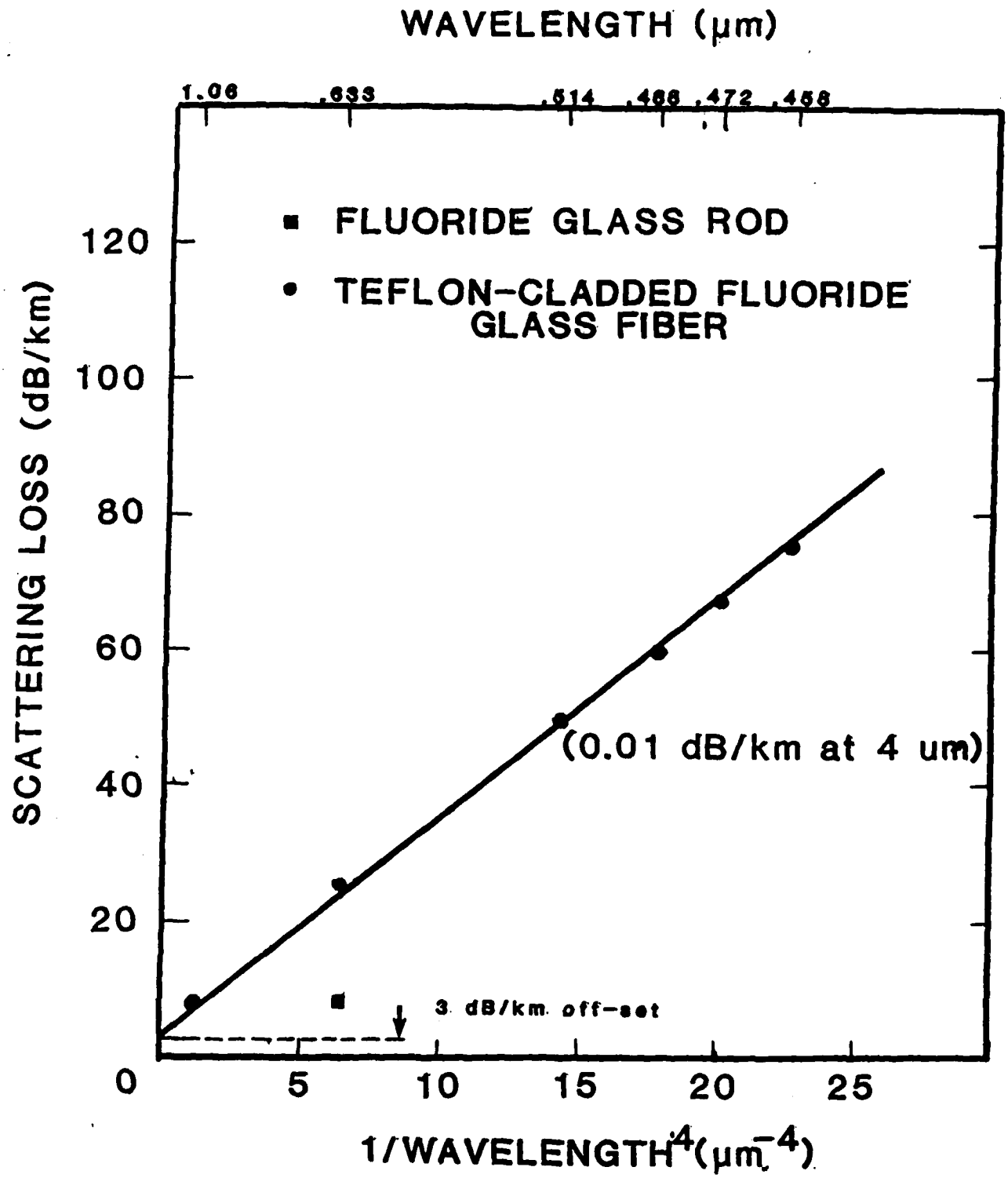
Figure Captions

Fig. 1 Scattering loss spectrum for a 51.53 $ZrF_4$ - 20.47 $BaF_2$ - 5.27 $LaF_3$ - 3.24 $AlF_3$ - 19.49 LiF glass.

Fig. 2 Scattering loss spectrum for a 51 $ZrF_4$ - 16 $BaF_2$ - 5 $LaF_3$ - 3 $AlF_3$ - 20 LiF - 5 $PbF_2$ teflon-cladded fiber. The 3 dB/km off-set is mainly due to interface scattering defects.


WAVELENGTH (nm)
633
458
18
16
14
12
10
8
6
4
2
0
SCATTERING LOSS (dB/km)
ZrF4-based glass
(0.0027 dB/km at 4 μm)
Suprasil 1
ZrF4-based glass
(theoretical limit[5])
5
10
15
20
25
30
1/WAVELENGTH4 (μm−4)


WAVELENGTH (μm)
1.06
.633
.514
.488
.472
.458
FLUORIDE GLASS ROD
TEFLON-CLADDED FLUORIDE GLASS FIBER
SCATTERING LOSS (dB/km)
120
100
80
60
40
20
0
(0.01 dB/km at 4 um)
3 dB/km off-set
5
10
15
20
25
1/WAVELENGTH$^4$(μm$^{-4}$)

# Minimization of OH absorption and scattering losses in zirconium fluoride glasses

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The most important criterion in maximizing the IR transparency of fluoride glasses for low-loss optical fiber applications is the elimination of the anionic impurities, mainly OH, which enter the glass during the batching and melting processes.[1] By analogy with the OH absorption coefficient in silica glass fiber, it was estimated that 1-ppm OH would give rise to a 5000-dB/km loss at 2.9 $\mu m^2$ in fluoride glass fibers. In addition, particle inclusions, phase separation, and submicron inhomogeneities or crystallization, which result in high scattering losses, must be totally suppressed. Previously the minimum OH absorption loss reported for a fluoride glass fiber was ~1000 dB/km at 2.9 $\mu m^2$, and the lowest scattering loss contribution for a fluoride glass rod was estimated to be 65 dB/km at 0.633 $\mu m$.[2] In this paper, substantially lower losses have been achieved using reactive atmosphere processing to remove OH and proper melting, refining, and quenching conditions to eliminate scattering imperfections.

Reactive atmosphere processing of zirconium fluoride-based glasses using $SF_6$, HF, $CCl_4$, $CF_4$, and $NH_4HF_2$ has been conducted. The extent of bulk OH removal determined as a function of reaction time, processing temperature, and gas flow rate has been studied. The effects of impurities, side reaction, and material degradation originating from the reactive atmosphere on the optical transparency of the fluoride glasses will be discussed. In Fig. 1, spectrum A shows an intensive absorption band corresponding to an ~78,000-dB/km loss at 3400 $cm^{-1}$ due to surface and bulk OH for a zirconium fluoride-based glass processed under an inert gas atmosphere. The effect of processing the same sample under an $SF_6$ reactive atmosphere is illustrated in spectrum B. The residual OH absorption band in curve B remained unchanged with sample thickness suggesting that essentially only surface OH remains after such processing.

The scattering losses in bulk fluorozirconate glasses have also been investigated as a function of melting and refining procedures, quenching rates, and fiber drawing temperatures. The scattering loss was measured using an Ar-ion laser and a He–Ne laser in conjunction with a silicon photodiode detector. The light signal from a small solid angle was detected as a function of scattering angle and wavelength. The measurement system was calibrated using benzene as a standard. Figure 2 illustrates the lowest scattering loss currently achieved for a zirconium fluoride glass, matching that of a high-purity Suprasil I and following a $\lambda^{-4}$ wavelength dependence characteristic of intrinsic Rayleigh scattering.

In summary, this paper reports advances in two areas essential for the development of high-transparency fluoride glass fibers, namely, OH removal and sharply reduced scattering losses. This has been achieved by utilization of both reactive $SF_6$ atmosphere processing as well as optimized thermal processing of the bulk glass. (13 min)

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# Minimization of OH absorption and scattering losses in zirconium fluoride glasses

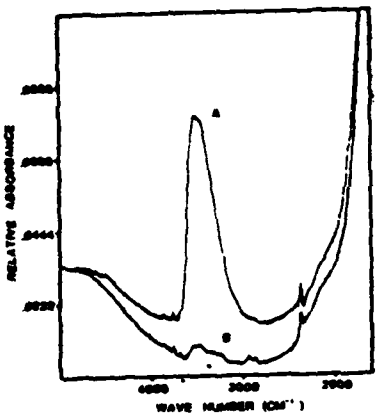


*Fig. 1. OH absorption of a 51.53 $ZrF_4$–20.47 $BaF_2$–5.27 $LaF_3$–3.24 $AlF_3$–19.49 LiF glass before and after an $SF_6$ reactive atmosphere processing.*

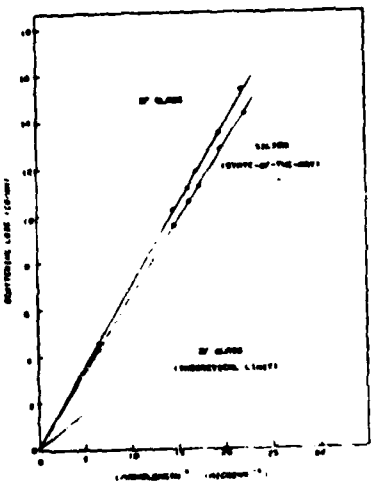

*Fig. 2. Rayleigh scattering of a 51.53 $ZrF_4$–20.47 $BaF_2$–5.27 $LaF_3$–3.24 $AlF_3$–19.49 LiF glass.*

# CHARACTERIZATION OF CRYSTALS IN FLUOROZIRCONATE GLASSES

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Extrinsic scattering due to the formation of crystallites is one of the factors which has prevented the theoretically predicted minimum loss from being attained in fluoride optical fibers. It is important to characterize these crystallites so that the processing parameters can be modified to avoid devitrification. For optical fiber research, it is more important to identify the first crystals which appear in the glass, rather than to simply characterize the final crystallization products in a mostly or totally crystallized sample. Even extemely low levels of crystallization such as $V_c < 10^{-10}$, where $V_c$ is the volume fraction crystallized, cannot be tolerated in ultra-low loss optical fibers.

In this study, the degree of crystallization of the $ZrF_4$-BaF-LiF-$AlF_3$-$LaF_3$ glass composition ranged from $V_c \simeq 10^{-6}$ to less than $10^{-10}$. The crystallites were analyzed by optical microscopy, micro X-ray diffraction, and SEM. Optical microscopy with transmitted polarized light was found to be the most useful technique for rapid characterization of the degree of crystallization and identification of the crystal habit. The electron image mode from the SEM was not found to be useful for such a low degree of crystallization. Without careful preparation, there was virtually no chance that a crystal could be found on the surface of the sample.

The analysis of fluorescent X-rays from the SEM was also found to be of limited value since lithium could not be detected, the lanthanum peaks were usually masked by the barium peaks, and the aluminum peak was partially masked by the large zirconium peak. Micro X-ray diffraction was found to be the most useful technique for identifying the crystalline phase. Particles as small as a few microns could be analyzed in a specially prepared X-ray diffractometer.

Many different crystallization products were observed to form from the same glass composition, depending on the processing conditions. Several of the common ones were analyzed in more detail. The cubic particle in Figure 1 was identified by micro X-ray diffraction as $AlF_3$, while the hexagonal platelet in Figure 2 was identified as $LaF_3$. The results are also consistent with SEM/EDAX analyses on isolated crystals and with birefringences reported in the literature.

Although many different crystals were observed over the course of the investigation, there were usually only one or two morphologies present in a given sample. These well-formed crystals grew during quenching and were not undissolved batch. Such monitoring of the crystallization products can show whether the high-temperature melting process has been sufficient to dissolve all crystals and whether the quenching rate is sufficiently high to prevent significant recrystallization.

The scattering coefficient of these crystals was calculated for a wavelength of 4 microns. It was assumed that the crystals were

spherical in shape. For relative refractive indices of $m = 0.9$ or $m = 1.1$, it was found that the scattering coefficient increased as $r^2$ (where r is the radius) over the range of particle sizes $r = 0.5$ microns to $r = 5$ microns. For small particles, the scattering coefficient was relatively independent of refractive index. For larger particles, the scattering coefficient increased dramatically when $m < 0.9$ or $m > 1.1$.

This study has found optical microscopy to be the most powerful tool in characterizing the state of crystallization of a glass suitable for optical fibers. With this knowledge of the crystallite size, number and morphology, the processing conditions can be modified to minimize crystallization.

# RAYLEIGH SCATTERING IN FLUORIDE GLASS OPTICAL FIBRES

*Indexing terms: Optical fibres, Scattering, Glasses*

The present study has verified for the first time the explicit $\lambda^{-4}$ Rayleigh behaviour of light scattering in fluoride glass optical fibres and has projected an ultra-low Rayleigh scattering loss of at least 0·012 dB/km at 4 μm.

*Introduction*: Recently, it was demonstrated that the measured light scattering loss in fluoride bulk glasses is indeed Rayleigh in character,[1,2] and in addition can be reduced to an ultra-low minimum of $2·7 \times 10^{-3}$ dB/km at 4 μm.[1] Scattering losses in fluoride glass fibres, on the other hand, have not yet been measured directly, but have been merely estimated from total fibre loss spectra.[3,4] These estimates can be sometimes erroneous since impurity absorption bands may easily distort the results. In addition, all fluoride fibre scattering loss data reported to date are substantially higher than in silica-based fibres,[3,4] and do not follow the explicit $\lambda^{-4}$ Rayleigh dependence but vary only as the inverse square of the wavelength.[3] This latter type of scattering was attributed to fibre inhomogeneities whose size is comparable to the wavelength of light.[3] In the present study, the direct measurement of scattering losses as a function of wavelength was carried out for the first time in fluoride glass fibres using an integrating sphere. Furthermore, the present investigation has verified for the first time the intrinsic Rayleigh behaviour of light scattering in fluoride glass fibres, and has projected an ultra-low Rayleigh scattering loss of at least 0·012 dB/km at 4 μm.

*Preparation of fluoride glass fibres*: Fluoride glass fibres were prepared from the highly stable $ZrF_4$-$BaF_2$-$LaF_3$-$LiF$-$AlF_3$-$PbF_4$ glass system[5] using the batching and melting procedure described earlier.[1,5] The fluoride melts were cast into moulds to form glass rods, 10 cm long and 1 cm in diameter, having a refractive index of 1·525. The rods were then coated with Teflon FEP and drawn into fibres using a resistance furnace. The drawing temperature was set at 303°C and the drawing speed was maintained at 5 m/min. The fibres obtained were generally 40 m long, 315 μm in overall diameter and 10 μm in polymer cladding thickness.

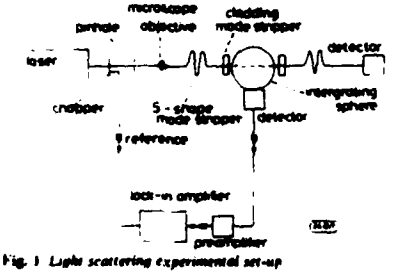


Fig. 1 *Light scattering experimental set-up*

*Direct measurement of fibre scattering losses*: Samples of fluoride glass fibre, each 1 m long, were randomly selected from a 40 m-long fibre for testing. The experimental set-up for light scattering measurement is shown in Fig. 1. Incident light from either an Argon-ion, He-Ne or Nd:YAG laser was chopped and launched through a pinhole, and was then focused onto the Teflon-clad fluoride glass fibre with a 10 × microscope objective (launch NA = 0·1). Cladding modes were suppressed by using S-shaped mode strippers and black strips of cloth saturated with index-matching oil. The scattered light was collected using an integrating sphere measuring 7 cm in diameter and containing a silicon-photodiode detector. Index-matching liquid droplets were placed on the fibre within the sphere to remove any scattered light trapped in the cladding, so that it would also be included in the measurement. To eliminate the light scattered and reflected back from the detector end of the fibre, the output end of the fibre was terminated in index-matching oil during the measurement. The light signal detected from the integrating sphere passed through a low-noise preamplifier and into a lock-in amplifier. The scattering loss was determined by first measuring the signal resulting from the scattered light $P_{sc}$ and then positioning the fibre output end within the sphere to measure the total power in the fibre $P_{tot}$. The scattering loss $\alpha_{sc}$ can then be calculated from[6,7]

$$\alpha_{sc}\ (\text{dB/km}) = \frac{4·34 \times 10^5}{L\ (\text{cm})} \frac{P_{sc}}{P_{tot}} \qquad (1)$$

where $L$ is the fibre length sampled which corresponds to the diameter of the sphere.

*Results and discussion*: Under a visible incident laser beam, the light scattered from the Teflon-clad fluoride glass fibre samples appeared visually identical to that of low-loss silica fibres, namely dim and homogeneous throughout the fibre. The fibre spectral scattering loss data are plotted in Fig. 2. A least-squares fit to the results indicates that the loss can be expressed as

$$\alpha_{sc}\ (\text{dB/km}) = 3·16/\lambda^4 + 5·08 \qquad (2)$$

where $3·16/\lambda^4$ (dB/km) represents the Rayleigh scattering loss contribution which projects to 0·012 dB/km at 4 μm, and where 5·08 dB/km represents the wavelength-independent scattering off-set which is due mainly to core-clad interface defects and partly to high-order cladding and leaky modes.

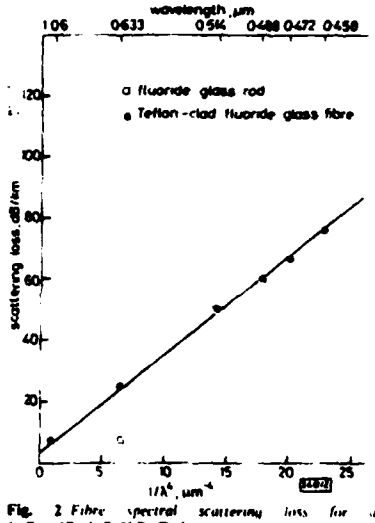


Fig. 2 *Fibre spectral scattering loss for a $ZrF_4$-$BaF_2$-$LaF_3$-$AlF_3$-$LiF$-$PbF_2$ Teflon-clad fibre*

Scattering loss measurement was also carried out for a fluoride glass rod, before it was covered with Teflon and drawn into fibres, using an experimental set-up described earlier.[1] As shown in Fig. 2, a bulk scattering loss of 7 dB/km was obtained at 0·6328 μm, which is about three times lower than the Rayleigh scattering loss observed in the drawn fibre. The data suggest the formation of fibre drawing induced scattering centres whose size is smaller than the wavelength of light. Such centres may originate at the core-clad boundary from surface roughness of the mechanically polished glass rod, and/or inside the bulk of the fibre itself because of the imposed drawing conditions, such as temperature and feed rate. Optimisation of drawing conditions should result in the further reduction of fibre scattering losses towards the bulk glass levels.

*Conclusions*: In summary, the present study has verified for the first time the Rayleigh character of light scattering losses in fluoride glass fibres. In addition the spectral Rayleigh scattering-loss data obtained for a Teflon-clad fluoride glass fibre, prepared from a highly stable $ZrF_4$-based glass system, project to an ultra-low loss of at least 0·012 dB/km at 4 μm.

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# FLUORIDE GLASS PREFORMS PREPARED BY A ROTATIONAL CASTING PROCESS

*Indexing terms: Optical fibres, fluoride glass*

A new approach has been developed to fabricate fluoride-glass-clad fibres from preforms having controlled core/clad ratios and uniform cladding thickness. In contrast to earlier casting methods, preform core/clad ratios remained unchanged over the entire length of all preforms. The new method also permits fabrication of much larger preforms.

*Introduction:* Since the discovery of $ZrF_4$-based glass in 1975,[1] the research and development in fluoride glass optical fibres has been growing at a rapid rate. Long-length unclad fibres can be prepared using the single crucible method or the cast-rod approach,[2-5] and Teflon-clad fibres can be obtained from the rod-Teflon FEP tube technique.[6] To date, fluoride-glass-clad fibres have only been successfully prepared from preforms fabricated by allowing the central part of the cladding melt in a mould to flow out and by casting the core melt into the tube thus obtained.[7-11] Preforms fabricated from this casting process typically display an undesirable tapering of core and cladding dimensions along the length of the cast tube assembly. In this letter, we report a new approach for preparing all fluoride glass fibres from preforms having high radial and longitudinal uniformity and selectively controlled core/clad ratios. In addition, this new method allows upscaling to large-size preforms while maintaining these desired preform dimensional characteristics.

**Table 1 CORE AND CLADDING FLUORIDE GLASS COMPOSITIONS**

| Glass composition | $ZrF_4$ | $BaF_2$ | $LaF_3$ | $AlF_3$ | LiF | $PbF_2$ |
|---|---|---|---|---|---|---|
| mole % | | | | | | |
| I | 53 | 19 | 5 | 3 | 20 | |
| II | 51·3 | 17 | 5 | 3 | 20 | 3·7 |
| III | 51 | 16 | 5 | 3 | 20 | 5 |

**Table 2 FLUORIDE GLASS PHYSICAL PROPERTIES**

| Glass compositions | Tg | Tx | $\alpha$ | $n$(at 0·63 μm) |
|---|---|---|---|---|
| | °C | °C | °C$^{-1}$ × 10$^{-7}$ | |
| I | 275 | 357 | 1·41(45–255°C) | 1·512 |
| II | 254 | 345 | | 1·517 |
| III | 257 | 360 | 1·34(45–195°C) | 1·525 |

*Method:* The core and cladding glass compositions and corresponding glass transition temperature (Tg), crystallisation temperature (Tx), expansion coefficient ($\alpha$), and refractive index ($n$) are listed in Tables 1 and 2. Fibre preforms were prepared from paired compositions I and II, II and III, and I and III; the last combination yielded the highest numerical aperture of 0·2. The fluoride glass samples were melted using technical grade fluorides in capped platinum crucibles under an argon atmosphere at 850°C for 60 min. A schematic diagram of the newly developed rotational casting process for fluoride glass preforms is illustrated in Fig. 1. The cladding glass melt was poured into a 6 in-long gold-coated cylindrical mould preheated at around Tg and was then rotated with an Emco Compact 5 lathe at speeds ≥ 3000 rev/min. A highly concentric fluoride cladding glass tube whose inner diameter was precisely controlled by the initial volume of injected glass was thus obtained. There was no detectable variation in wall thickness along the entire length of the tube, and no bubbles were observed. Alternatively, such a fluoride glass tubing can be prepared by melting directly in the rotating mould followed by a rapid quench to Tg and a final annealing step. The core glass was next transferred to the tube either by pouring the melt down a fluoride glass bait rod or by dipping the tube into the core melt in order to avoid bubble formation. A cross-sectional photograph of a preform thus prepared is shown in Fig. 2. A preform step-index profile obtained from a York Technology Model P101 Preform Analyser is illustrated in Fig. 3.

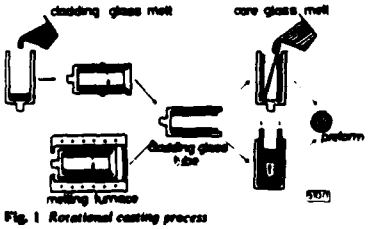


Fig. 1 *Rotational casting process*

Fluoride-glass-clad preforms were drawn into fibres using a resistance ring furnace with a localised heat zone about 7 mm long. The drawing speed was around 40 m/min and the drawing temperature was set at 315 ± 5°C. Long-length fluoride glass fibres of core diameters and cladding thicknesses ranging from 70–150 μm and from 10–30 μm, respectively, were actually prepared. The optical loss in these fibres was presently as high as 6 dB/m at 3·6 μm due to water, metal impurities in the technical grade fluoride raw materials, and drawing induced scattering defects. The impurity concentration of the glass in ppm, determined with a Spectra-Matrics DC Argon Plasma Spectra-Span IIIB is Fe(1·6), Cu(0·58), Eu(1·82), Sm(0·82), Ce(3·9) and Tb(< 0·5). Fibre losses are expected to improve dramatically with proper control of fibre drawing parameters, and with the use of high-purity starting materials and controlled atmospheric melting and drawing. For the most part, the purpose of the work reported here was to develop and demonstrate the new preform fabrication process.

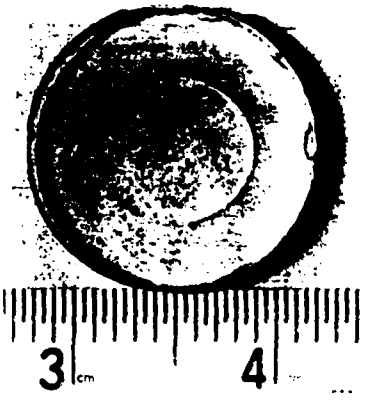


Fig. 2 *Cross-sectional photograph of a preform of compositions I and III*

Core diameter = 7·75 mm, cladding thickness = 3·25 mm, NA = 0·2

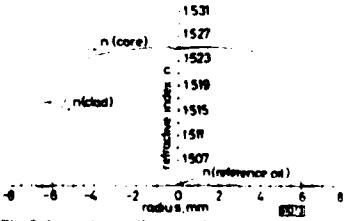


Fig. 3 *Step-index profile of a preform of compositions II and III*

Core diameter = 10·6 mm, cladding thickness = 0·7 mm, NA = 0·156, index of reference oil = 1·503

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*Conclusion*: It has been demonstrated that the rotational casting process can be employed to prepare fluoride glass fibre preforms having a uniform and controlled core-clad ratio. The new technique permits for the first time the preparation of large fluoride glass preforms essential for the future fabrication of long distance repeaterless data links.

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*12th May 1982*

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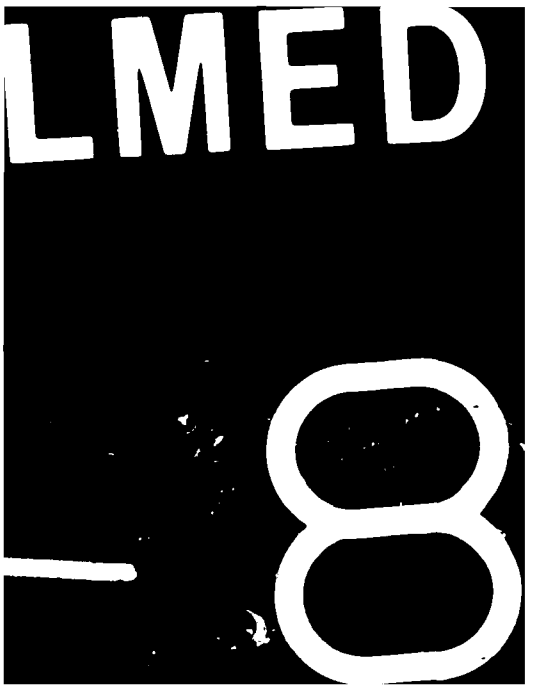
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